# Electronic properties of the crystalline phases of the Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system

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The electronic properties of the crystalline phases of the Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system are investigated both experimentally and theoretically. Experimental data obtained by x-ray photoelectron spectroscopy and <sup>121</sup>Sb Mössbauer spectroscopy are reported and analyzed from tight-binding calculations, which are used here because of the complexity of the materials. The main features of the x-ray photoelectron valence bands and S  $K\beta$  emission spectra are identified. The binding energy of the S  $2p_{3/2}$  core level is found to decrease from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>2</sub>S in agreement with the variations of the calculated S charges. We show that the <sup>121</sup>Sb Mössbauer isomer shift and the surface of the prepeak observed in x-ray-absorption spectra at the Sb  $L_{III}$  edge can be linearly correlated because they are both strongly dependent on the Sb 5*s* electron population. Finally, analytical expressions of the numbers of Sb and S valence electrons are derived from simple molecular calculations. These expressions provide rather simple explanations for the observed main trends in the variations of the experimental results in terms of local structural changes. [S0163-1829(97)06543-0]

#### I. INTRODUCTION

Ternary chalcogenides of thallium form an interesting family of materials because of their potential optoelectronic applications. Many studies concern layered compounds of the form  $TlAB_2$ , where *A* stands for an element of columns III or V and *B* represents a chalcogen. For example physical properties of  $TlInS_2$ ,<sup>1,2</sup>  $TlInSe_2$ ,<sup>2,3</sup>  $TlGaS_2$ ,<sup>2,3</sup>  $TlGaSe_2$ ,<sup>3,4</sup> and  $TlSbS_2$  (Ref. 5) have been extensively investigated because of the structural anisotropy of these materials. There is also a particular interest for compounds of the form  $Tl_3AB_3$ .<sup>6</sup> For example,  $Tl_3ASSe_3$  has been proposed as a candidate for nonlinear optical and acousto-optic applications.<sup>7</sup> The interesting results obtained for these two classes of materials suggest further investigations in other thallium chalcogenides.

This paper concerns the crystalline phases of the  $Sb_2S_3$ - $Tl_2S$  system. Previous works have unambiguously shown the existence of four ternary crystalline phases:<sup>8–11</sup>  $TlSb_5S_8$ ,  $TlSb_3S_5$ ,  $TlSbS_2$ , and  $Tl_3SbS_3$ . Their structures are rather complex showing different crystallographic sites for each of the three atoms. The Sb atoms are found to be surrounded by three, four, or five S atoms as nearest neighbors. The local environments of the Tl atoms are more complex in relation with their ionic character. From the chemist's point of view, addition of  $Tl_2S$  to  $Sb_2S_3$  increases the covalent character of the Sb-S bonds and decreases the ionic character of the Tl-S bonds. This can be related to changes in the dimensionality of the antimony compounds from  $Sb_2S_3$ , which is a chainlike compound to  $Tl_3SbS_3$ , which can be described by a three-dimensional network.<sup>12</sup>

The electronic properties of the ternary compounds have been partially investigated. The x-ray-absorption spectroscopy (XAS) at the Sb  $L_{III}$  edge has been used to study the contribution of the Sb 5*s* states to the conduction bands of the glassy and crystalline compounds of the As<sub>2</sub>S<sub>3</sub>-Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system.<sup>13</sup> The XAS spectra exhibit a prepeak at the absorption edge, which has been attributed to the Sb 5*s* empty states. The prepeak amplitude is found to increase from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>3</sub>SbS<sub>3</sub> indicating an increase in the contribution of the Sb 5*s* empty states. The S  $K\beta$  x-ray-emission spectroscopy (XES) has been used to investigate the S 3*p* valence-band states.<sup>14</sup> The XES spectra are formed by a broad asymmetric band. The width of this band decreases and a well-resolved shoulder occurs at the low transitionenergy side with increasing content of Tl atoms. The results obtained from these two experiments have been qualitatively explained from changes in the local environments of Sb and S atoms, respectively.

In this paper we report new experimental results obtained by x-ray-photoemission spectroscopy (XPS) and <sup>121</sup>Sb Mössbauer spectroscopy. These results as well as those obtained by XAS and XES are discussed from a tight-binding method. This approach is used here because of the complexity of the crystalline phases of the system Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S. In addition, tight-binding theory has been shown to provide correct variations in the electronic properties of very different materials including chalcogenides.<sup>15-19</sup> The main features of the valence bands obtained by XPS and S  $K\beta$  XES are analyzed from the contributions of the atomic orbitals. Variations of the core-level binding energies measured by XPS are found to be consistent with changes in the calculated atomic charges. Finally, we show that variations of the <sup>121</sup>Sb Mössbauer isomer shift and the surface of the prepeak observed in XAS spectra at the Sb  $L_{\rm III}$  edge can be correlated because they are both strongly dependent on the Sb 5s electron population.

We focus our interest on the effect of structural changes

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TlSb<sub>5</sub>S<sub>8</sub><sup>b</sup> TISbS2d  $Tl_2S^f$ Sb<sub>2</sub>S<sub>3</sub><sup>a</sup> TlSb<sub>3</sub>S<sub>5</sub><sup>c</sup> Tl<sub>3</sub>SbS<sub>3</sub><sup>e</sup> Monoclinic Monoclinic Triclinic Orthorhombic Rhombohedral Rhombohedral Space groups Pnma Pn  $P2_1/c$ P1R3m *R*3 21 81  $N_{\rm at}$ 20 56 36 16 <sup>a</sup>Reference 20. <sup>b</sup>Reference 8. <sup>c</sup>Reference 9.

TABLE I. Space groups and numbers of atoms per cell  $N_{\rm at}$  of the crystalline phases of the Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system.

in the local environments of Sb and S atoms onto the electronic properties. Molecular calculations are proposed in order to relate the numbers of valence electrons for these two atoms to their local environments. Considering only the main interatomic interactions we have derived simple analytical expressions that are able to explain the main trends in the local electronic properties in terms of atom coordination numbers and bond lengths.

<sup>d</sup>Reference 10. <sup>e</sup>Reference 11. <sup>f</sup>Reference 21.

Section II concerns the synthesis and some structural aspects of the crystalline phases of the  $Sb_2S_3$ - $Tl_2S$  system. Experimental aspects of the XPS and Mössbauer measurements are given in Sec. III. The tight-binding scheme used in this paper is detailed in Sec. IV. The experimental data are reported and analyzed in Sec. V. The observed main trends in the variations of the local electronic properties are discussed in terms of the Sb and S environments from simple molecular calculations in Sec. VI. Finally, Sec. VII is devoted to conclusions.

### **II. SYNTHESIS AND STRUCTURES**

The crystalline phases of the Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system were prepared by direct synthesis in fused silica tubes evacuated to about  $10^{-5}$  Torr. Sb<sub>2</sub>S<sub>3</sub> was obtained from high-purity Sb and S elements heated to about 600 °C for about 1 week and then slowly cooled. Tl<sub>2</sub>S was prepared from Tl and S elements under Ar atmosphere in order to avoid oxydation. The melt was heated during 3 days and slowly cooled. TISbS<sub>2</sub> and Tl<sub>3</sub>SbS<sub>3</sub> were obtained from Tl<sub>2</sub>S and Sb<sub>2</sub>S<sub>3</sub> heated during 3 days at a temperature of about 500 and 600 °C, respectively.  $TlSb_3S_6$  was obtained from  $Sb_2S_3$  and  $TlSbS_2$  at a temperature of 380 °C for 3 weeks followed by a slow cooling. For  $TlSb_5S_8$  a glass with the same composition was first prepared by quenching a melt of Sb<sub>2</sub>S<sub>3</sub> and Tl<sub>3</sub>SbS<sub>5</sub> in water. The crystalline phase was obtained by annealing the glass at 254 °C for 3 weeks. All the compounds were finely grounded for the experimental studies and their structures were controlled by x-ray diffraction.

All the crystalline structures have been determined<sup>8-11,20,21</sup> and the main informations used for the analysis of the experimental data are reported in Table I. This table shows that the structural complexity of the materials is mainly due to the great number of atoms per unit cell and to the low lattice symmetry.

 $Sb_2S_3$  is a ribbonlike material formed by  $(Sb_4S_6)_n$  chains parallel to the *c* axis.<sup>20</sup> The  $Sb_4S_6$  units are formed by two

SbS<sub>3</sub> trigonal pyramids and two SbS<sub>5</sub> square base pyramids connected by threefold coordinated S atoms. The Sb<sub>4</sub>S<sub>6</sub> units are linked by twofold coordinated S atoms and form the  $(Sb_4S_6)_n$  chains. There are two and three distinct crystallographic sites for Sb and S, respectively. TlSb<sub>5</sub>S<sub>8</sub> is formed by  $(Sb_5S_8)_n$  double layers parallel to the (101) axis.<sup>8</sup> There are ten different crystallographic sites for the Sb atoms, which are in very distorded octahedral environments and are in fact surrounded by three, four, and five S atoms as nearest neighbors. There are 16 sites for the S atoms, which are strongly bounded to two or three Sb atoms. The layers are connected by long Sb-S bonds (>3.37 Å) and via Tl atoms. The Tl atoms occupy two different crystallographic sites and are surrounded by more than eight S atoms, suggesting a strong ionic character for the Tl-S bonds. TlSb<sub>3</sub>S<sub>5</sub> is a layered compound.<sup>9</sup> There are one, three, and five different crystallographic sites for Tl, Sb, and S, respectively. Two Sb sites are surrounded by three S atoms in trigonal pyramidal environments, the third Sb site forms a trigonal bipyramid with four S atoms. These SbS<sub>3</sub> and SbS<sub>4</sub> units form infinite layers connected by the longest Sb-S bonds of the bipyramids (2.85 Å). The Tl atoms are found in the layers and are surrounded by eight S atoms. TISbS<sub>2</sub> is a layered compound.<sup>10</sup> Each layer is formed by covalent chains containing Sb and S atoms which are linked together by long Sb-S bonds (3.7 Å)and ionic TI-S bonds (3.4 Å). The chains are built up from SbS<sub>4</sub> distorted trigonal bipyramids connected by two twofold coordinated S atoms. There are two, two, and four different crystallographic sites for Sb, Tl, and S, respectively. The structure of Tl<sub>3</sub>SbS<sub>3</sub> can be described by a hexagonal close packing of Tl and S atoms with intercalated Sb atoms.<sup>11</sup> The structure is rhombohedral and each atom occupies one crystallographic site. The Sb atoms are surrounded by three S atoms as nearest neighbors that form SbS<sub>3</sub> trigonal pyramids. The SbS<sub>3</sub> units are linked together by S-Tl-S bridges and form a three-dimensional network because of the partial covalent character of the Tl-S bonds. Tl<sub>2</sub>S is a distorted hexagonal close-packed arrangement of Tl atoms in which the octahedral intertices between pairs of planes of Tl atoms are occupied by S atoms.<sup>21</sup> The structure is rhombohedral. There are six and five different crystallographic sites for Tl and S, respectively. The Tl atoms are surrounded by three S atoms at distances in the range 2.5–3.3 Å, suggesting a more covalent character for the Tl-S bonds in Tl<sub>2</sub>S than in ternary compounds.

FIG. 1. Schematic description of the basic  $SbS_n$  units found in the crystalline phases of the  $Sb_2S_3$ - $Tl_2S$  system. The units are trigonal pyramids  $SbS_3$ , trigonal bipyramids  $SbS_4$ , and square base pyramids  $SbS_5$ .

The previous description of the crystalline structures shows that the local environments of the Sb atoms can be described by  $SbS_n$  units with n=3 (trigonal pyramids), n =4 (trigonal bipyramids), and n=5 (square base pyramids) (Fig. 1). The numbers of  $SbS_n$  units and the average Sb-S bond lengths of the antimony compounds studied in this paper are given in Table II. It is worth noticing that the values of the average Sb-S bond lengths are close to the sum of the covalent radii defined by Pauling<sup>22</sup> (2.4 Å). The average Sb-S bond length decreases from 2.62 Å (Sb<sub>2</sub>S<sub>3</sub>) to 2.43 Å (Tl<sub>3</sub>SbS<sub>3</sub>), suggesting a slight increase in the covalency of the Sb-S bonds with increasing Tl<sub>2</sub>S content. The values of the average Tl-S bond lengths are close to the sum of the ionic radii defined by Pauling<sup>22</sup> (3.3 Å) and decrease from 3.25 Å (TlSb<sub>5</sub>S<sub>8</sub>) to 2.87 Å (Tl<sub>2</sub>S), suggesting a decrease in the ionicity of the TI-S bonds. In fact the situation is more complicated for Tl<sub>3</sub>SbS<sub>3</sub> and Tl<sub>2</sub>S because the average Tl-S bond lengths of 3.03 Å and 2.87 Å, respectively, indicate a partial covalent character for the TI-S bonds. This is consistent with the observed low coordination number for the Tl atoms in these two compounds (3-5) compared with the Tl coordination numbers in the other three ternary compounds (5–7). In the six crystalline phases the  $SbS_n$  units are connected by twofold and threefold coordinated S atoms in order to form covalent networks.

### **III. EXPERIMENTS**

The XPS is used to obtain information on the binding energies of the core levels and on the densities of states (DOS) of the valence bands. The photoelectron spectra were excited by using a Mg anode x-ray tube ( $h\nu$ =1253.6 eV) and analyzed with an electrostatic hemispherical analyzer in the FAT (fixed analyzer transmission) mode. The spectrometer resolution was estimated from the Ag  $3d_{5/2}$  energy to be 0.8 eV. Since our compounds are insulators, a charging effect was observed that induced a shift of the photoelectron spectra towards a higher binding-energy scale. This effect was corrected by shifting the binding-energy scale in order to set the C 1s peak due to the superficial hydrocarbonated contamination to 285.0 eV. In these conditions the origin of the binding-energy scale corresponds to the Fermi level of the sample. In the case of samples containing Tl atoms the excitation of the Tl  $5d_{3/2,5/2}$  core levels at binding energies of about 13–15 eV by Mg K $\alpha$  satellite lines, namely, K $\alpha_3$ ,  $K\alpha'$ , and  $K\alpha_4$ , gives lower-intensity peaks that are precisely located in the energy range of the valence band. Consequently, a correction was achieved to subtract these contributions from the total photoelectron spectra. Because the samples were powders and due to the low values of the photoemission cross sections for Sb and Tl valence states, we obtained XPS valence-band spectra of low intensity.

The <sup>121</sup>Sb Mössbauer spectroscopy measurements were performed with a Elscint AME 40 spectrometer at liquid-Helium temperature for both the absorber and the source. A 500  $\mu$ Ci source of 37.2 keV  $\gamma$  rays was obtained from Ba <sup>121</sup>SnO<sub>3</sub>. The absorbing materials were obtained from powdered samples mixed with Apiezon jelly (grease) and containing approximately 1 mg/cm<sup>2</sup> of <sup>121</sup>Sb. The spectra were recorded during one day for a good signal-to-noise ratio. The velocity calibration was obtained by using a <sup>57</sup>Co source and a high-purity iron foil absorber. The Mössbauer parameters: isomer shift  $\delta$ , quadrupole splitting  $\Delta$ , and linewidth  $\Gamma$  were obtained by a nonlinear least-squares fit of the Mössbauer spectra with the computer program of Ruebenbauer and Birchall.<sup>23</sup>

The S K $\beta$  XES measurements were carried out at LURE (Orsay, France) in order to probe the partial S 3*p* density of states. The XAS spectra at the Sb  $L_{III}$  edge were recorded using the synchrotron radiation of the DCI storage ring (Orsay, France). Details on the measurements and a qualitative discussion of the results can be found elsewhere.<sup>13,14</sup> The results obtained from these two techniques are considered in this paper for a complete discussion in relation with the XPS and Mössbauer data. It is worth noticing that all the experiments were carried out on the same powdered samples.

TABLE II. Average Sb-S interatomic distances (in Å) and numbers of SbS<sub>n</sub> units (in parentheses) for the crystalline phases of the Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system. The SbS<sub>n</sub> units are trigonal pyramids SbS<sub>3</sub> (tp), trigonal bipyramids SbS<sub>4</sub> (tb), and square base pyramids SbS<sub>5</sub> (sp). The values of the Sb coordination numbers and the Sb-S interatomic distances averaged over the different SbS<sub>n</sub> units are given by  $n_{av}$  and  $d_{av}$ (Sb-S), respectively. The average Tl-S distance is given by  $d_{av}$ (Tl-S).

	tp	tb	sp	n <sub>av</sub>	$d_{av}(Sb-S)$	$d_{av}(Tl-S)$
Sb <sub>2</sub> S <sub>3</sub>	2.53 (1)		2.70 (1)	4	2.62	
TlSb <sub>5</sub> S <sub>8</sub>	2.48 (6)	2.62 (3)	2.67 (1)	3.5	2.55	3.25
TlSb <sub>3</sub> S <sub>5</sub>	2.50 (2)	2.61 (1)		3.33	2.54	3.17
TlSbS <sub>2</sub>		2.60 (2)		4	2.60	3.17
Tl <sub>3</sub> SbS <sub>3</sub>	2.43 (1)			3	2.43	3.03
$Tl_2S$						2.87

# **IV. THEORETICAL APPROACH**

We propose an analysis of the experimental data based on a tight-binding scheme following the procedure of Slater and Koster.<sup>24</sup> This approach can be easily applied to complex systems and has been shown to provide correct trends in the electronic properties of chalcogenide materials.<sup>16-18</sup> The one-electron Schrödinger equation is solved by developing the wave functions in a basis of Bloch orbitals that are written in terms of symmetrically orthogonalized atomic orbitals (Löwdin orbitals). Because of the orthogonality of these pseudoatomic orbitals the energy levels E and the wave functions  $\Psi$  are the eigenvalues and the eigenvectors of the Hamiltonian matrix, respectively. The dimension of the Hamiltonian matrix is equal to the total number of atomic orbitals in the unit cell. A minimal basis set including valence s and p orbitals are considered in the present work. Thus, the dimension of the matrix is  $4N_{at}$ , where  $N_{at}$  is the number of atoms in the unit cell ranging from 16 for TISbS<sub>2</sub> to 81 for Tl<sub>2</sub>S. The elements of the Hamiltonian matrix can be written as

$$H_{i\alpha,j\beta} = \sum_{l} e^{i\mathbf{k}(\mathbf{R}_{\beta} + \mathbf{R}_{l} - \mathbf{R}_{\alpha})} h_{i\alpha,j\beta}(l)$$
(1)

with

$$h_{i\alpha,j\beta}(l) = \int \varphi_{i\alpha}^*(\mathbf{r} - \mathbf{R}_{\alpha}) H \varphi_{j\beta}(\mathbf{r} - \mathbf{R}_{\beta} - \mathbf{R}_l), \qquad (2)$$

where i,j refer to atomic orbitals  $(s,p_x,p_y,p_z)$ ,  $\mathbf{R}_{\alpha}$ ,  $\mathbf{R}_{\beta}$  are the positions in the unit cell of the atoms denoted by  $\alpha$  and  $\beta$ , respectively, and  $\mathbf{R}_l$  is the vector of the Bravais lattice between the unit cells where are located the atoms  $\alpha$  and  $\beta$ , respectively. The summation in Eq. (1) is performed over several crystal cells because of the strong decrease of  $h_{i\alpha,j\beta}(l)$  with  $\mathbf{R}_l$ .

Following the idea of Slater and Koster the integrals  $h_{i\alpha,j\beta}(l)$  are not calculated but considered as adjustable tight-binding parameters. Two types of parameters are usually distinguished: the intra-atomic parameters that concern orbitals located on the same atom  $(l=1, \alpha=\beta)$  and the interatomic parameters involving orbitals on different atoms.

As a first approximation, the values of the free-atom energy can be used for the intra-atomic terms  $h_{i\alpha,i\alpha}(l)$ . However, large deviations are expected in some cases due to the orthogonalization procedure of the Löwdin orbitals as pointed out previously for oxyde compounds.<sup>19</sup> For Sb<sub>2</sub>S<sub>3</sub> a correct agreement between the XPS spectrum and the calculated DOS is obtained with the values of the free-atom en-Skillman:<sup>25</sup> Hermann ergy evaluated by and  $E_{3s}(S) = -20.8 \text{ eV}, \quad E_{3p}(S) = -10.27 \text{ eV}, \quad E_{5s}(Sb) = -14.8$ eV, and  $E_{5p}(Sb) = -7.24$  eV. For Tl<sub>2</sub>S the following intraatomic energies are used for Tl atoms:  $E_{5s}$ (Tl)=-13.92 eV and  $E_{5p}(\text{Tl}) = -4.61 \text{ eV}$ . The Tl 5s level has been shifted downwards from the value calculated by Hermann and Skillman for a correct agreement between the XPS valence band and calculated DOS. These intra-atomic parameters that provide correct DOS for Sb<sub>2</sub>S<sub>3</sub> and Tl<sub>2</sub>S have been transferred to the ternary compounds.

A two-center approximation is considered for the evaluation of the interatomic terms  $h_{i\alpha,j\beta}(l)$ , which are written in terms of the diatomic molecular interactions  $ss\sigma$ ,  $sp\sigma$ ,  $pp\sigma$ , and  $pp\pi$  obtained by empirical rules. Harrison<sup>15</sup> has proposed a  $d^{-2}$  rule, where *d* is the interatomic distance, which provides correct electronic structures for covalent materials when only nearest-neighbor interactions are considered. Interactions between more distant neighbors decrease more strongly than expected by a  $d^{-2}$  rule and a better evaluation is obtained by an exponential scaling law as proposed by Robertson.<sup>16</sup> Because of the bond-length distributions in the chalcogenide materials studied in this paper such an exponential scaling law is used here:

$$h_{i\alpha,j\beta}(l) = \frac{\hbar^2}{m} \frac{\eta_{ij}}{R_{\alpha\beta}^2} \exp\left[-\alpha_{ij}\left(\frac{d_{\alpha\beta}(l)}{R_{\alpha\beta}} - 1\right)\right], \quad (3)$$

where  $R_{\alpha\beta}$  is the sum of the covalent radii for the atoms  $\alpha$  and  $\beta$  as defined by Pauling,<sup>22</sup>  $d_{\alpha\beta}(l)$  is the distance between the atoms  $\alpha$  and  $\beta$ , and  $\eta_{ij}$  are the Harrison parameters:<sup>26</sup>  $\eta_{ss\sigma} = -1.32$  eV,  $\eta_{sp\sigma} = 1.42$  eV,  $\eta_{pp\sigma} = 2.22$ eV,  $\eta_{pp\pi} = -0.63$  eV, and  $\alpha_{ij} = 3$ . Equation (3) was used to evaluate the Sb-S and Tl-S interactions with bond lengths smaller than about 3 and 3.6 Å, respectively. Interactions between more distant atoms have been neglected because of their small values.

The present analysis of the experimental data requires the evaluation of the DOS and the atomic charges from the calculated energy levels and wave functions. The partial DOS for the orbital  $\varphi_{i\alpha}$  is defined by

$$n_{i\alpha}(E) = \sum_{n,\mathbf{k}} |\langle \varphi_{i\alpha} | \Psi_{n,\mathbf{k}} \rangle|^2 \,\delta(E - E_{\mathbf{n},\mathbf{k}}), \tag{4}$$

where *n* and **k** denote band index and wave vector, respectively. The sum runs over the  $4N_{\text{at}}$  bands for *n* and a grid of points in the first Brillouin zone for **k**. The total DOS is obtained by summation of the  $n_{i\alpha}(E)$  over all the orbitals  $\varphi_{i\alpha}$ :

$$n(E) = \sum_{n,\mathbf{k}} \delta(E - E_{n,\mathbf{k}}).$$
(5)

The densities of states obtained from Eqs. (4) and (5) are convoluted with a Gaussian of width equal to 1 eV for a comparison with XPS and XES spectra. The number of electrons *i* on the atom  $\alpha$  can be evaluated by integration of  $n_{i\alpha}(E)$  over the valence band:

$$N_{i\alpha} = 2\sum_{n,\mathbf{k}} |\langle \varphi_{i\alpha} | \psi_{n,\mathbf{k}} \rangle|^2.$$
(6)

Finally, the charge on the atom  $\alpha$  is defined as the difference between the numbers of valence electrons on the free atom  $Z_{\alpha}$  and on this atom in the solid:

$$Q_{\alpha} = Z_{\alpha} - \sum_{i} N_{i\alpha}, \qquad (7)$$

where the summation runs over the valence orbitals  $\varphi_{i\alpha}$  of the atom  $\alpha$ .



FIG. 2. XPS valence band (dotted line), S  $K\beta$  XES spectrum, and calculated DOS for Sb<sub>2</sub>S<sub>3</sub>. The total DOS n(E) and the partial DOS for Sb and S atoms are shown. For the partial DOS the dashed and solid lines correspond to *s* and *p* states, respectively.

# V. RESULTS AND DISCUSSION

### A. Valence bands

The XPS valence bands, S K $\beta$  XES spectra and calculated DOS of the six crystalline phases of the Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system are shown in Figs. 2–7. The origin of energies is taken at the top of the calculated valence bands. Except for Sb<sub>2</sub>S<sub>3</sub> the XPS valence bands are plotted for energies greater than -10 eV since the Tl 4*d* core level at about -15 eV hides the lower part of the valence bands. The XPS valence bands are compared to the total DOS and analyzed from the partial DOS. The XES spectra are compared to the S 3*p* partial DOS.

The valence-band spectrum of  $Sb_2S_3$  exhibits a broad band between -16 and -6 eV labeled I and an asymmetric



FIG. 3. XPS valence band (dotted line), S  $K\beta$  XES spectrum and calculated DOS for Tl<sub>2</sub>S. The total DOS n(E) and the partial DOS for Tl and S atoms are shown. For the partial DOS the dashed and solid lines correspond to *s* and *p* states, respectively.



FIG. 4. XPS valence band (dotted line), S  $K\beta$  XES spectrum and calculated DOS for TlSb<sub>5</sub>S<sub>8</sub>. The total DOS n(E) and the partial DOS for Sb, Tl, and S atoms are shown. For the partial DOS the dashed and solid lines correspond to *s* and *p* states, respectively.

peak for energies greater than -5 eV labeled II (Fig 2). Similar results have been obtained by Leonhardt et al.27 From the partial DOS one can see that the lower-energy part of the peak I labeled Ia has a strong S 3s character. The upper energy part Ib has a Sb 5s character due to interactions between this orbital and the sulfur valence orbitals. The peak II has a strong S 3p character that results from interactions between S 3p and Sb 5p orbitals (IIa) but has also a lonepair character (IIb). The shoulder IIc is due to interactions between S 3p and Sb 5s orbitals. The XES spectrum shows a broad and asymmetric band that reflects the S 3p partial DOS. The main contribution comes from the S 3p lone-pair states ( $\approx -1$  eV). The asymmetry of the XES band is due to interactions between S 3p and Sb 5p orbitals ( $\approx -4$  eV). Because of its strong S 3p character the main peak II of the XPS spectrum is similar to the XES band.



FIG. 5. Same as Fig. 4 for  $TlSb_3S_5$ .



FIG. 6. Same as Fig. 4 for  $TlSbS_2$ .

The XPS valence-band spectrum of Tl<sub>2</sub>S is shown in Fig. 3 and is similar to that obtained by Porte et Tranquard.<sup>28</sup> The valence band is formed by two peaks at about -6 and -2 eV labeled I and II, respectively. Peak I has a Tl 6s character resulting from interactions between Tl 6s and S 3p orbitals. Peak II has a strong S 3p character due to weak interactions between S 3p and Tl 6p orbitals (IIa) and between S 3p and Tl 6s orbitals (IIb). The XES spectrum shows a main band at -2 eV and a shoulder at about -6 eV. These two structures occur at the same energies as the two main peaks I and II of the XPS spectrum and correspond to the S 3p contribution of the states involved in these two peaks. It is worth noticing that the two peaks observed in the XPS valence band have nearly the same amplitudes whereas the structures of the XES spectrum have very different intensities since only the peak II has a strong S 3p character. Finally, the peak due to the S 3s states, which is predicted at about -14 eV is not seen in the XPS spectrum because it is hidden by the Tl 4dcore level.



FIG. 7. Same as Fig. 4 for Tl<sub>3</sub>SbS<sub>3</sub>.

TABLE III. Binding energies and full widths at half maximum (in parentheses) of the S  $2p_{3/2}$ , Tl  $4f_{7/2}$ , and Sb  $4d_{5/2}$  core levels measured by XPS. All values are given in eV.

	S 2p <sub>3/2</sub>	Tl $4f_{7/2}$	Sb 4 <i>d</i> <sub>5/2</sub>
Sb <sub>2</sub> S <sub>3</sub>	161.3 (1.6)		33.1 (1.4)
TlSb <sub>5</sub> S <sub>8</sub>	161.3 (1.7)	118.2 (1.6)	33.1 (1.6)
TlSb <sub>3</sub> S <sub>5</sub>	161.2 (1.6)	118.1 (1.4)	33.0 (1.5)
TlSbS <sub>2</sub>	161.1 (1.5)	118.1 (1.3)	32.9 (1.2)
Tl <sub>3</sub> SbS <sub>3</sub>	160.9 (1.5)	118.2 (1.5)	32.9 (1.2)
$Tl_2S$	160.3 (0.7)	117.8 (0.9)	

The XPS valence band spectra of the ternary compounds show an asymmetric and featureless broad band for energies greater than -6 eV labeled I (Figs. 4–7) similar to that observed for Sb<sub>2</sub>S<sub>3</sub> in the same energy range. The width of this band is found to decrease with increasing Tl<sub>2</sub>S content. The XES spectra also show an asymmetric and broad band which follows the same trend.<sup>14</sup> The XES spectrum of Tl<sub>3</sub>SbS<sub>3</sub> exhibits an additional small peak at about -5 eV and looks like that of Tl<sub>2</sub>S whereas the XES spectra of the other ternary compounds are similar to that of Sb<sub>2</sub>S<sub>3</sub>. The partial DOS show that the main band I of the XPS spectra has a S 3pcharacter. This band results from interactions between S 3pand Sb 5p orbitals for energies at about -3 eV (Ia) and exhibits a S 3p nonbonding character for energies at about -1 eV (Ib). We explain the decrease in the widths of the main XPS and XES peaks from TlSb<sub>5</sub>S<sub>8</sub> to Tl<sub>3</sub>SbS<sub>3</sub> by the decrease in the amplitude of the DOS structure Ia in relation with the decrease in the number of Sb-S bonds. The observed shoulder in the XES spectrum of  $Tl_3SbS_3$  at about -5 eV is attributed to interactions between S 3p and Tl 6s orbitals. The small influence of the Tl 6s states in the XES spectra of the other ternary compounds can be explained by the small values of the TI-S interactions compared with those of the Sb-S interactions and by the low value of the ratio [T1]/[Sb] which varies from 0.2 for TlSb<sub>5</sub>S<sub>8</sub> to 1 for TlSbS<sub>2</sub>. The absence of a well-resolved peak in the XPS spectra for the Tl 6s states should be related to the low value of the free-atom photoemission cross section for these states compared to those of the other atoms.<sup>29</sup>

### **B.** Core levels

The values of the binding energies and the linewidths of the S  $2p_{3/2}$ , Tl  $4f_{7/2}$ , and Sb  $4d_{5/2}$  core levels measured by XPS are given in Table III. One can observe a decrease in the S  $2p_{3/2}$  binding energy,  $E_b(S)$ , from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>2</sub>S, which suggests a decrease in the sulfur charge. We have evaluated the charges Q(S) on the S atoms from Eq. (5) averaged over the different crystallographic sites. The values of Q(S) are given in Table IV and a quasilinear correlation between  $E_b(S)$  and Q(S) is obtained (Fig. 8). In order to clarify the effect of the Tl atoms upon the S charges another calculation was carried out which included ionic Tl<sup>+</sup> cations. This was obtained by neglecting the Tl-S interactions since the Tl 6s free-atom energy level is located in the valence

TABLE IV. Average values of the Sb 5s,  $N_{5s}(Sb)$ , S 3s,  $N_{3s}(S)$ , and Tl 6s,  $N_{6s}(Tl)$ , numbers of electrons and average values of the atomic charges Q. The values of the S charges obtained from calculations including Tl-S interactions, Q(S), or neglecting them, Q'(S), are given.

	$N_{5s}(Sb)$	Q(Sb)	$N_{3s}(\mathbf{S})$	Q(S)	Q'(S)	$N_{6s}(\mathrm{Tl})$	$Q(\mathrm{Tl})$
Sb <sub>2</sub> S <sub>3</sub>	1.9446	1.47	1.959	-0.980	-0.980		
TlSb <sub>5</sub> S <sub>8</sub>	1.9380	1.43	1.956	-0.973	-1.013	1.992	0.63
TlSb <sub>3</sub> S <sub>5</sub>	1.9365	1.45	1.955	-0.985	-1.056	1.988	0.58
TlSbS <sub>2</sub>	1.9358	1.43	1.953	-1.015	-1.191	1.990	0.60
Tl <sub>3</sub> SbS <sub>3</sub>	1.9250	1.37	1.954	-1.091	-1.431	1.991	0.63
Tl <sub>2</sub> S			1.951	-1.213	-2	1.991	0.62

band and the Tl 6p free-atom energy level in the conduction band. The results also show a decrease of the charges Q(S)'from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>2</sub>S (Fig. 8). Significant quantitative differences with the previous calculation is observed especially for Tl<sub>3</sub>SbS<sub>3</sub> and TlSbS<sub>2</sub>. The charges on the Tl atoms decrease when Tl-S interactions are taken into account leading to an increase of the S charges by an amount of about 0.35[T1]/[S], where the brackets denote the atomic concentrations. Although the Tl atoms strongly influence the S charges it is worth noticing that both calculations predict the correct trends in the variations of  $E_b(S)$ . In addition, these two calculations provide similar values for the Sb charges indicating that Tl-S interactions have negligible effects on the electronic population of this atom. The values of the Tl  $4f_{7/2}$  and Sb  $4d_{5/2}$  binding energies (Table III) do not vary noticeably and are found within experimental errors  $(\pm 0.1 \text{ eV})$  except for the Tl  $4f_{7/2}$  binding energy of Tl<sub>2</sub>S, which is slightly lower (0.3 eV) than the other values. The absence of significant variations could be explained from the small changes in the calculated atomic charges (<0.1) and because Sb and Tl are heavy atoms.

# C. <sup>121</sup>Sb Mössbauer spectroscopy

A typical <sup>121</sup>Sb Mössbauer spectrum is shown in Fig. 9 for TlSb<sub>5</sub>S<sub>8</sub> and rather similar spectra are obtained for the other antimony compounds. They all exhibit a broad band ( $\approx$ 10 mm/s) due to the eight allowed nuclear transitions for



FIG. 8. Correlations between the experimental values of the S  $2p_{3/2}$  core-level binding energy and the charges on S calculated with TI-S interactions (squares) and without TI-S interactions (circles). 1, Sb<sub>2</sub>S<sub>3</sub>; 2, TISb<sub>5</sub>S<sub>8</sub>; 3, TISb<sub>3</sub>S<sub>5</sub>; 4, TISbS<sub>2</sub>; 5, TI<sub>3</sub>SbS<sub>3</sub>; 6, TI<sub>2</sub>S.

Sb. Thus, the contributions of the different crystallographic sites occupied by the Sb atoms cannot be detected and only one site has been considered in the fitting procedure of the spectra.

The values of the isomer shift  $\delta$ , the quadrupole splitting  $\Delta$ , and the linewidth  $\Gamma$  are given in Table V. The values of  $\Delta$  are found in the range 10.8–12.7 mm/s suggesting a strong anisotropy of the Sb local environments in agreement with the structural description (Table II). The low value of  $\Gamma$  for Tl<sub>3</sub>SbS<sub>3</sub> (1.2 mm/s) compared with the values obtained for the other antimony compounds (1.4–1.7 mm/s) is consistent with the existence of only one crystallographic site for the Sb atoms in Tl<sub>3</sub>SbS<sub>3</sub>.

The values of the <sup>121</sup>Sb Mössbauer isomer shift  $\delta$  are characteristic of Sb<sup>3+</sup> cations<sup>30</sup> as proposed from a previous structural analysis.<sup>12</sup> They are found to increase from Sb<sub>2</sub>S<sub>3</sub> (-6.03 mm/s) to Tl<sub>3</sub>SbS<sub>3</sub> (-3.14 mm/s). In order to analyze the evolution of  $\delta$  we consider the usual expression,<sup>30</sup>

$$\delta = \alpha_{\text{nuc}}[\rho_a(0) - \rho_s(0)], \qquad (8)$$

where  $\alpha_{nuc}$  is a nuclear constant,  $\rho_a$  and  $\rho_s$  are the electron densities at the nucleus in the absorber and in the source, respectively. The nuclear constant  $\alpha_{nuc}$  is a function of the relative change in the radius of the nuclear states involved,  $\Delta R/R$ , which is negative for Sb.<sup>30</sup> Thus, the observed in-



FIG. 9.  $^{121}$ Sb Mössbauer spectrum of TlSb<sub>5</sub>S<sub>8</sub>. The velocity scale is referenced to InSb material.

TABLE V. <sup>121</sup>Sb Mössbauer parameters relative to InSb. Values of the Mössbauer isomer shift  $\delta$ , the quadrupole splitting  $\Delta$ , and the full width at half maximum  $\Gamma$  are given in mm/s.

	δ	Δ	Г
Sb <sub>2</sub> S <sub>3</sub>	-6.03	10.8	1.42
TlSb <sub>5</sub> S <sub>8</sub>	-5.09	12.0	1.55
TlSb <sub>3</sub> S <sub>5</sub>	-4.57	12.5	1.70
TlSbS <sub>2</sub>	-4.26	12.7	1.61
Tl <sub>3</sub> SbS <sub>3</sub>	-3.14	11.1	1.19

crease of  $\delta$  from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>3</sub>SbS<sub>3</sub> suggests a decrease of  $\rho_a(0)$ . An accurate evaluation of the electronic density at the nucleus is rather difficult for solids with complex structures. However, variations of  $\rho_a(0)$  are mainly dependent on changes in the number of Sb 5*s* electrons,  $N_{5s}(Sb)$ , and to a lesser extent on changes in the number of Sb 5*p* electrons,  $N_{5p}(Sb)$ . As a first approximation  $\rho_a(0)$  is expected to vary linearly with  $N_{5s}(Sb)$ .<sup>18</sup> The tight-binding calculations give  $N_{5s}(Sb)\approx 2$  for the different antimony compounds but a small decrease of  $N_{5s}(Sb)$  from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>3</sub>SbS<sub>3</sub> is obtained (Table IV). The observed linear correlation between the experimental values of  $\delta$  and the calculated values of  $N_{5s}(Sb)$  confirms the main influence of the Sb 5*s* electrons on the Mössbauer isomer shift (Fig. 10).

### D. X-ray absorption spectroscopy

The XAS at the Sb  $L_{\rm III}$  edge has been recently used to investigate the local structure in the crystalline and glassy phases of the Sb<sub>2</sub>S<sub>3</sub>-As<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system.<sup>13</sup> The electronic transitions from the inner Sb  $2p_{3/2}$  core level to the Sb empty states that obey selection rules (*s*-type and *d*-type final states) were concerned. The spectra clearly exhibit a peak at about 4137 eV whose the amplitude increases from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>3</sub>SbS<sub>3</sub>. This peak occurs at the absorption edge and can be attributed to the empty Sb 5*s* states localized at the bottom of the conduction band.

The number of Sb 5*s* electrons,  $N_{5s}$ (Sb), is obtained by integration over the valence band of the partial DOS including the spin degeneracy  $2n_{5s,Sb}(E)$ . Thus, integration of



FIG. 10. Variations of the experimental <sup>121</sup>Sb Mössbauer isomer shift  $\delta$  as a function of the calculated number of Sb 5*s* electrons  $N_s$ (Sb). The straight line is obtained by linear regression. The numbering is the same as in Fig. 8.



FIG. 11. Variations of the surface of the first XAS peak at the  $L_{\text{III}}$  edge of Sb (in arbitrary units) as a function of the calculated number of Sb 5*s* electrons  $N_s$ (Sb). The straight line is obtained by linear regression. The numbering is the same as in Fig. 8.

 $2n_{5s,Sb}(E)$  over the conduction band gives  $2-N_{5s}(Sb)$ . We assume that the transition probability between the Sb  $2p_{3/2}$ core level and the Sb 5s empty states does not vary noticeably with energy. This means that the surface of the observed XAS peak should vary as  $2-N_{5s}$  (Sb). We have evaluated the surface  $S_p$  of this peak from the XAS spectra by considering as boundary values:  $S_p = 0$  for  $Sb_2S_3$  and  $S_p = 1$  for  $Tl_3SbS_3$ . As expected, a linear correlation between the values of  $S_p$ and the calculated values of  $N_{5s}$  (Sb) is found (Fig. 11). Since the <sup>121</sup>Sb Mössbauer isomer shift  $\delta$  varies linearly with  $N_{5s}(Sb)$ , a linear correlation between  $S_p$  and  $\delta$  is obtained that can be explained by the strong influence of the Sb 5selectrons upon these two experimental parameters (Fig. 12). These results show that the combined application of XAS and <sup>121</sup>Sb Mössbauer spectroscopy provides very interesting information for the study of antimony compounds.

### VI. LOCAL ELECTRONIC STRUCTURES

### A. Sb atoms

In the preceding section it has been shown that tightbinding calculations provide a correct analysis of the experimental electronic structures of the crystalline phases of the  $Sb_2S_3$ -Tl<sub>2</sub>S system. The experimental results obtained by XPS (core levels), XAS, and Mössbauer spectroscopy have



FIG. 12. Linear correlation between the surface of the first XAS peak at the  $L_{\rm III}$  edge of Sb (in arbitrary units) and the <sup>121</sup>Sb Mössbauer isomer shift. The numbering is the same as in Fig. 8.

been correlated to the calculated numbers of electrons. In this section, we propose simple molecular calculations in order to relate the electronic populations to the local atomic environments by simple analytical expressions.

We first describe the approximations used for the molecular calculations of the electronic populations on Sb atoms. First, we only consider the dominant  $pp\sigma$  interactions between Sb and S nearest neighbors. The other molecular interactions  $(ss\sigma, sp\sigma, pp\pi)$  and the  $pp\sigma$  interactions between the other pairs of atoms are neglected. Second, we take the Sb-S-Sb angles equal to 90°. In this case, the S atoms have less than three Sb nearest neighbors in orthogonal directions and there are only interactions between Sb 5porbitals and combinations of S 3p orbitals pointing towards the Sb atoms. With these two approximations the crystals behave as a set of isolated  $SbS_n$  units with negative charges and Tl<sup>+</sup> ions. The electronic structures of the ternary phases are formed by the molecular levels of the  $SbS_n$  units and the atomic levels of Tl<sup>+</sup>. The main effect of the other interactions is to broaden these levels into bands as obtained from the tight-binding calculations of Sec. V.

As shown by Eq. (6) the number of electrons  $N_{i\alpha}$  is obtained from the projection of the electronic wave functions onto the atomic orbital  $\varphi_{i\alpha}$ . Since there are no interactions involving the Sb 5s orbitals in the present molecular model we have  $N_{5s}(Sb) = 2$ . The evaluation of  $N_{5p}(Sb)$  requires the calculation of the wave functions for the  $SbS_n$  molecules. In order to obtain a simple analytical expression for  $N_{5p}(Sb)$ the S-Sb-S angles that are found in the range  $76^{\circ}-108^{\circ}$  are taken to be equal to 90°. In this case the  $SbS_n$  units can be described by (6-n) Sb-S diatomic molecules and (n-3)S-Sb-S linear molecules. There are no interactions between these molecules which are found in three orthogonal directions. The analytical expressions of the energy levels and wave functions can be easily derived for these simple molecules. The electronic structure of a Sb-S molecule is formed by a pair of bonding/antibonding states resulting from interactions between S 3p and Sb 5p orbitals. The electronic structure of a S-Sb-S molecule is formed by a nonbonding S 3p state and a pair of bonding/antibonding states arising from interactions between Sb 5p orbitals and a combination of 3p orbitals of the two S atoms. The number of Sb 5pelectrons is obtained from the Sb 5p contribution of the bonding states since they are always found in the valence band. We consider for simplicity that all the Sb-S bond lengths within a  $SbS_n$  molecule are equal to the average value d. In this case  $N_{5p}(Sb)$  can be evaluated from the contributions of the Sb 5p electrons of the Sb-S molecules,  $N_{5p}(Sb)'$ , and of the S-Sb-S molecules,  $N_{5p}(Sb)''$ . This gives

$$N_{5p}(Sb) = (6-n)N_{5p}(Sb)' + (n-3)N_{5p}(Sb)''.$$
 (9)

The contribution of the diatomic molecules to the number of Sb 5p electrons is given by

$$N_{5n}(\mathrm{Sb})' = 1 - \alpha' \tag{10}$$

with

$$\alpha' = \frac{\gamma}{\sqrt{1+\gamma^2}},\tag{11}$$

$$\gamma = \frac{E_{5p}(\mathrm{Sb}) - E_{3p}(\mathrm{S})}{2\beta},\tag{12}$$

where  $E_{5p}$  (Sb) and  $E_{3p}$ (S) are the intra-atomic energies and  $\beta$  denotes the  $pp\sigma$  interaction between Sb and S atoms as defined by Eq. (3). Following the idea of Harrison<sup>15</sup> concerning  $sp^3$  covalent semiconductors, the term  $\alpha'$  given by Eq. (11) can be viewed as the Sb-S bond polarity neglecting the effects of the *s* orbitals. The term  $\gamma$  is the ratio between the heteropolar term  $E_{5p}$ (Sb)- $E_{3p}$ (S) and the homopolar term  $2\beta$ , which can both be compared to the two parts of the average band gap as defined by Phillips.<sup>31</sup> This can be viewed as a measure of the ionocovalent character of the Sb-S bond. Depending on the value of  $\gamma$  the polarity  $\alpha'$  varies between -1 and +1. These two values of  $\alpha'$  correspond to complete electronic transfers (ionic bonds) whereas for  $\alpha=0$  the bond is covalent. For the Sb-S bonds found in the SbS<sub>n</sub> molecules the polarity is of about 0.5.

In the same way, we can evaluate the contribution of the S-Sb-S molecules to the number of Sb 5p electrons:

$$N_{5n}(Sb)''=1-\alpha''$$
 (13)

with

$$\alpha'' = \frac{\gamma}{\sqrt{2 + \gamma^2}},\tag{14}$$

where  $\gamma$  is defined by Eq. (12). The coefficient  $\alpha''$  can also be defined as a polarity coefficient but for the electronic tranfer between the central Sb atom and the two S atoms of the S-Sb-S molecule. This coefficient varies from 0.4 to 0.6 as the Sb-S distance increases from 2.5 to 3 Å.

The number of Sb 5*p* electrons can be written in terms of the polarity coefficients  $\alpha'$  and  $\alpha''$  from Eqs. (9), (10), and (13):

$$N_{5p}(Sb) = 3 + 3(\alpha'' - 2\alpha') + n(\alpha' - \alpha'').$$
(15)

Putting the expressions (11), (12), and (14) in Eq. (15) yields an analytical but rather complex expression for  $N_{5p}$ (Sb) in terms of the Sb coordination, the average Sb-S bond length and the free-atom energy values of Sb and S. This expression can be simplified by considering the small variations of the average Sb-S bond length *d* within each SbS<sub>n</sub> unit (Table II). The expressions (11) and (14) of the bond polarities are expanded in Taylor series around  $d_0 = 2.4$  Å (sum of the Sb and S covalent radii) in terms of  $\Delta d = d - d_0$ . This gives for Eq. (15)

$$N_{5n}(\mathrm{Sb}) \approx 1.28 - 1.58\Delta d + n(0.12 + 0.08\Delta d).$$
 (16)

The second and third terms of the right side of this equation have opposite signs. Since *d* increases by about 0.3 Å as *n* increases from 3 to 5 (Table II) these two terms tend to cancel each other. Evaluation of Eq. (16) for the different  $\text{SbS}_n$  units of the antimony compounds gives  $N_{5p}(\text{Sb}) = 1.6 \pm 0.1$ . Thus, the values of the Sb charges,  $Q(\text{Sb}) \approx 1.4$ , are in close agreement with those obtained by the tight-binding calculations of Sec. V (Table IV). This simple molecular model shows that charges on Sb do not vary noticeably for the The preceding molecular model predicts a population of two 5*s* electrons on Sb, independently of the Sb coordination because interactions involving the Sb 5*s* orbitals have been neglected. The tight-binding calculations of Sec. V have given similar results although a small decrease of  $N_{5s}$ (Sb) from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>3</sub>SbS<sub>3</sub> has been found and correlated to the observed increase of the Mössbauer isomer shift  $\delta$ . In order to clarify the influence of the local structural changes around the Sb atoms onto the variations of  $\delta$  an analytical expression of  $N_{5s}$ (Sb) is derived. Following the idea of Lefebvre *et al.*<sup>18</sup> we propose an evaluation of  $N_{5s}$ (Sb) for the Sb atoms of the Sb<sub>n</sub> molecules from a simple perturbation theory.

Let us first calculate the number of Sb 5*s* electrons,  $N_{5s}(Sb)'$ , in a S<sub>1</sub>-Sb-S<sub>2</sub> linear asymmetric molecule. The  $pp\sigma$  interactions are written  $\beta_1, \beta_2$  and the  $sp\sigma$  interactions  $\Delta_1, \Delta_2$ , where the indices 1 and 2 denote the Sb-S<sub>1</sub> and Sb-S<sub>2</sub> bonds, respectively. The zeroth-order approximation to the molecular wave functions is obtained from the preceding molecular model. The  $sp\sigma$  interactions are introduced by an evaluation of the molecular wave functions at first order. We obtain

$$N_{5s}(Sb)' = 2 - \frac{a^2}{[E_a - E_{5s}(Sb)]^2} \frac{(\beta_1 \Delta_1 - \beta_2 \Delta_2)^2}{\beta^2}$$
(17)

with

$$a^{2} = 1 - \frac{1/2}{1 + \gamma^{2} - \gamma(\gamma^{2} + 1)^{1/2}},$$

$$E_{a} = E_{5p}(Sb) - \beta\gamma + \beta(\gamma^{2} + 1)^{1/2},$$

$$\gamma = \frac{E_{5p}(Sb) - E_{3p}(S)}{2\beta},$$

$$\beta^{2} = \beta_{1}^{2} + \beta_{2}^{2}.$$

Considering the exponential bond-length dependence of the hopping integrals  $\Delta$  and  $\beta$  given by Eq. (3), it can be shown that  $a/[E_a-E_{5s}(Sb)]$  varies slightly with the Sb-S bond length *d* and that

$$2 - N_{5s}(Sb)' \sim 1 - e^{6(d_1 - d_2)/d_0}, \tag{18}$$

where  $d_1$  and  $d_2$  are the bond lengths of the Sb-S<sub>1</sub> and Sb-S<sub>2</sub> molecules, respectively, and  $d_0 = 2.4$  Å is the sum of the Sb and S covalent radii. For  $d_1 = d_2$  Eq. (18) shows that  $N_{5s}$ (Sb)' is equal to 2, indicating that in this case the S<sub>1</sub>-Sb-S<sub>2</sub> molecules do not contribute to changes in  $N_{5s}$ (Sb)'. For  $d_1 \neq d_2$  the contribution of the S<sub>1</sub>-Sb-S<sub>2</sub> molecules to  $2 - N_{5s}$ (Sb)' increases with the asymmetry of the molecules. If the difference between  $d_1$  and  $d_2$  is greater than about 1 Å the influence of the most distant S atom can be neglected and the molecule is equivalent to a diatomic molecule. For distances smaller than 1 Å the contribution of the asymmetric S<sub>1</sub>-Sb-S<sub>2</sub> molecules is found to be always smaller than that of the Sb-S molecules of the same SbS<sub>n</sub> unit. Thus, the S<sub>1</sub>-Sb-S<sub>2</sub> molecules do not contribute noticeably to  $N_{5s}(Sb)'$ , which mainly depends on the contributions of the diatomic molecules. By using Eq. (17) for the Sb-S molecules one obtains

$$2 - N_{5s}(\text{Sb})' \approx \frac{a^2 \Delta^2}{[E_a - E_{5s}(\text{Sb})]^2}.$$
 (19)

We use Eq. (3) for  $\Delta$  and values of the tight-binding parameters given in Sec. IV. The term  $a/[E_a - E_{5s}(\text{Sb})]$  does not vary noticeably with the Sb-S bond length and can be expanded in Taylor series at first order in  $\Delta d = d - d_0$ . This gives for Eq. (19)

$$2 - N_{5s}(\mathrm{Sb})' \approx (0.024 - 0.013\Delta d) e^{-2.5\Delta d}.$$
 (20)

The number of Sb 5*s* electrons for a SbS<sub>*n*</sub> molecule,  $N_{5s}$ (Sb), is obtained from the contributions of the (6-n)Sb-S molecules given by Eq. (20). For simplicity we consider that all the Sb-S interatomic distances within a SbS<sub>*n*</sub> molecule have the same average value *d* since they do not vary by more than 0.15 Å. The number of Sb 5*s* electrons is given by

$$N_{5s}(Sb) \approx 2 - (6 - n)(0.056 - 0.013d)e^{-2.5d + 6}$$
. (21)

This expression shows that increases in the Sb coordination number *n* and in the Sb-S bond length *d* both tend to decrease  $N_{5s}$ (Sb). In addition,  $N_{5s}$ (Sb) is strongly dependent on the Sb coordination number *n* which varies from 3 to 5 and to a lesser extent on the average Sb-S bond length *d*, which varies by less than 0.15 Å. Considering for simplicity that d=2.5 Å, we obtain

$$N_{5s}(Sb) \approx 1.890 + 0.018n.$$
 (22)

For a crystal, the number of Sb 5s electrons is obtained by averaging the values of  $N_{5s}$  (Sb) obtained by Eq. (22) over the different Sb sites. This gives the same expression as Eq. (22) but with the average Sb coordination number  $n_{av}$  given in Table II instead of n. From  $Sb_2S_3$  to  $Tl_3SbS_3 n_{av}$  is found to decrease from 4 to 3 leading to a decrease of  $N_{5s}$ (Sb) from 1.962 to 1.946. These values are greater than those obtained from the tight-binding calculations of Sec. V (Table IV) by about 0.02 electron but the same trend is observed except for TlSbS<sub>2</sub>, which has the same average coordination as  $Sb_2S_3$ . This can be due to the simplicity of the present molecular model. However, this calculation clearly shows that the observed main trends in the variations of the Mössbauer isomer shift and the surface of the first XAS peak, which both strongly depend on  $N_{5s}(Sb)$ , can be roughly explained by the changes in the Sb coordination number.

#### B. S atoms

It has been shown in Sec. V that the S  $2p_{3/2}$  binding energy decreases from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>2</sub>S consistently with the decrease of the average sulfur charges evaluated by tightbinding calculations (including or not including Tl-S interactions). In order to relate these changes to the local environments of the S atoms, we propose a molecular calculation with the same basic approximations as in Sec. VI A. We only consider  $pp\sigma$  interactions between S and Sb nearest neighbors and the Sb-S-Sb angles are taken to be equal to 90°. Interactions with Tl atoms are neglected and these atoms are



FIG. 13. Schematic description of the local environments of the S atoms for the crystalline phases of the Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system. The molecules are of the form  $SSb_nS_{n'}$  with  $n \le 3$  and  $n' \le n$ . Only, the  $SSb_3S_3$  molecule is shown for clarity. The other  $SSb_nS_{n'}$  molecules may be drawn from this figure by eliminating (3-n) Sb and (3-n') S atoms.

assumed to be ionic (Tl<sup>+</sup>). This approximation has a noticeable effect on the values of the S charges but not on their variations as shown in Sec. V. Since there are no interactions with the S 3s orbitals in the present model the S atoms have two 3s electrons in correct agreement with the tight-binding calculations of Sec. V, which give  $N_{5s}(S) \approx 1.96$  electron for the different compositions (Table IV). This can be explained by the deep S 3s atomic level compared with the values of the other atomic levels involved in calculations. The evaluation of the number of S 3p electrons,  $N_{3p}(S)$ , requires the determination of the molecules describing the S local environments. The S atoms are surrounded by less than three Sb nearest neighbors. Because the Sb coordination number is greater or equal to 3 the other S atoms included in linear S-Sb-S molecules have to be taken into account. Thus, the molecules are of the form  $SSb_nS_{n'}$ , where  $n \leq 3$  is the S coordination number and  $n' \leq n$  is the number of linear S-Sb-S molecules. A schematic description is given in Fig. 13 and the different S environments found in the materials studied in this paper are reported in Table VI. Because all the bond angles are assumed to be proportional to 90°, there are no interactions between the  $SSb_nS_{n'}$  molecules. In addition, the  $SSb_nS_{n'}$  molecules are formed by n' linear S-Sb-S molecules and (n-n') S-Sb molecules in three orthogonal directions. The electronic structure of the  $SSb_nS_{n'}$  molecules is formed by the molecular levels of the noninteracting S-Sb and S-Sb-S molecules. Thus,  $N_{3p}(S)$  can be evaluated from the S 3*p* contributions to the bonding states of the (n-n')

S-Sb molecules,  $N_{3s}(S)'$ , and of the n' S-Sb-S molecules,  $N_{3p}(S)''$ , and from the contribution of the S 3*p* electrons to the nonbonding states: 6-2n. If we consider for simplicity that all the Sb-S bond lengths within a SSb<sub>n</sub>S<sub>n'</sub> molecule have the same average bond length *d*, we obtain

$$N_{3p}(\mathbf{S}) = 6 - 2n + (n - n')N_{3p}(\mathbf{S})' + n'N_{3p}(\mathbf{S})'' \quad (23)$$

with

$$N_{3p}(S)' = 1 + \alpha',$$
 (24)

$$N_{3p}(\mathbf{S})'' = 2 - \frac{1}{2 + \gamma^2 + \gamma(\gamma^2 + 2)^{1/2}},$$
 (25)

where  $\alpha'$  and  $\gamma$  are given by Eqs. (11) and (12), respectively. As for the SbS<sub>n</sub> units, we expand Eqs. (24) and (25) in Taylor series around  $d_0 = 2.4$  Å in terms of  $\Delta d = d - d_0$ , which depends on the environment of the S atoms (Table VI). The resulting first-order approximation to Eq. (23) reads

$$N_{3p}(S) \approx 6 - n(0.54 - 0.45\Delta d) + n'(0.21 - 0.26\Delta d).$$
(26)

This expression shows that the number of S 3p electrons increases slightly with the average bond length (because  $\Delta d = 0 - 0.3$  Å) and decreases with the S coordination number n and the number of S-Sb-S molecules n'. The average number of S 3p electrons in a crystal is obtained by summation of the  $N_{3p}(S)$  over the different S environments given in Table VI. By neglecting the variations of d over the different  $SSb_nS_{n'}$  units of a crystal we obtain the same expression as Eq. (26) but with the average values  $n_{\rm av}, n'_{\rm av}$  and  $\Delta d_{\rm av} = d_{\rm av}$  $-d_0$  instead of n,n' and  $\Delta d$ , respectively. These values as well as the calculated values of the average S charges,  $Q_{\rm av}(S)$ , are given in Table VI. Comparison between the S charges, Q'(S), obtained by the tight-binding calculations of Sec. V without Tl-S interactions (Table IV) and  $Q_{av}(S)$ shows a good agreement (<0.1 electron). Thus, molecular and tight-binding calculations provide similar variations of the S charges which are consistent with the variations of the S  $2p_{3/2}$  binding energy. The present molecular calculation shows that the observed decrease in the S  $2p_{3/2}$  binding energy from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>2</sub>S can be explained by the decrease in the average S coordination number  $n_{av}$  which is the leading parameter in Eq. (26). However, it is clear that the partial covalent character of the Tl-S bonds, which are not taken into account in this simple model, tends to reduce this effect as shown in Sec. V.

TABLE VI. Structural information for the molecular calculation of the charge on S:  $Q_{av}(S)$ . The average Sb-S interatomic distances (in Å) and the numbers of  $SSb_nS_{n'}$  molecules (in parentheses) are given for the different crystalline phases. The values of the Sb-S interatomic distances, *n* and *n'* averaged over the different  $SSb_nS_{n'}$  units are given by  $d_{av}$ ,  $n_{av}$ , and  $n'_{av}$ , respectively.

	$SSb_1S_0$	$SSb_2S_0$	$SSb_2S_1$	$SSb_3S_1$	SSb <sub>3</sub> S <sub>2</sub>	$d_{\rm av}$	$n_{\rm av}$	$n'_{\rm av}$	$Q_{\rm av}(S)$
Sb <sub>2</sub> S <sub>3</sub>		2.46 (1)			2.71 (2)	2.63	2.67	1.33	-1.03
TlSb <sub>5</sub> S <sub>8</sub>		2.49 (8)	2.63 (5)	2.64 (1)	2.70 (2)	2.57	2.19	0.63	-1.09
TlSb <sub>3</sub> S <sub>5</sub>		2.52 (3)	2.64 (2)			2.57	2	0.45	-1.14
TlSbS <sub>2</sub>			2.66 (4)			2.66	2	1	-1.30
Tl <sub>3</sub> SbS <sub>3</sub>	2.44 (1)					2.44	1	0	-1.48

# VII. CONCLUSIONS

The electronic properties of the crystalline phases of the Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system have been studied by XPS and Mössbauer spectroscopies. These results as well as previous results obtained by S K $\beta$  XES and XAS have been explained from tight-binding calculations that take into account the real and complex structure of the materials. The main features of the XPS valence bands and XES spectra have been analyzed in terms of atomic orbital contributions. The variations of the XPS core levels, the <sup>121</sup>Sb Mössbauer isomer shift and the XAS prepeak surface have been correlated to changes in the calculated numbers of valence electrons. It has been shown that the <sup>121</sup>Sb Mössbauer isomer shift and the surface of the XAS prepeak at the Sb  $L_{III}$  edge can be linearly correlated because they both strongly depend on the number of Sb 5selectrons. Simple molecular models have been proposed to relate the experimental data to the local structure. The observed increases in the <sup>121</sup>Sb Mössbauer isomer shift and in the surface of the XAS prepeak at the Sb  $L_{\rm III}$  edge from

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Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>3</sub>SbS<sub>3</sub> have been explained from the decrease of the Sb coordination number. The variations of the Sb  $4d_{5/2}$ binding energy have been found to be very small because of the opposite influences of the Sb coordination number and the Sb-S bond lengths. The observed decrease in the S  $2p_{3/2}$ binding energy from Sb<sub>2</sub>S<sub>3</sub> to Tl<sub>3</sub>SbS<sub>3</sub> has been related to the decrease of the average S coordination number. Thus, tightbinding calculations and molecular models provide a coherent picture of the observed main trends in the variations of the electronic properties of the crystalline phases of the Sb<sub>2</sub>S<sub>3</sub>-Tl<sub>2</sub>S system.

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